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(54) Title: CONDITIONING SHAMPOO COMPOSITIONS

(57) Abstract

Disclosed is a conditioning shampoo composition comprising by weight: (a) from about 0.05 % to about 50 % of a polyhydrophilic anionic surfactant; (b) from about 0.05 % to about 20 % of a cationic conditioning agent selected from the group consisting of cationic surfactants, cationic polymers, and mixtures thereof; (c) from about 0.2 % to about 20 % of a cationic silicone emulsion comprising by weight of the cationic silicone emulsion from about 2 % to about 20 % of a cationic surfactant; and an emulsifiable amount of a silicone compound having a particle size of less than about 50 microns; and (d) an aqueous carrier.

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CONDITIONING SHAMPOO COMPOSITIONS

TECHNICAL FIELD

The present invention relates to conditioning shampoo compositions which both cleanse the hair and condition the hair.

BACKGROUND

Human hair becomes soiled due to its contact with the surrounding environment and from the sebum secreted by the scalp. The soiling of hair causes it to have a dirty feel and an unattractive appearance. The soiling of the hair necessitates shampooing with frequent regularity.

Shampooing cleans the hair by removing excess soil and sebum. However, shampooing can leave the hair in a wet, tangled, and generally unmanageable state. Once the hair dries, it is often left in a dry, rough, lusterless, or frizzy condition due to removal of the hair's natural oils and other natural conditioning and moisturizing components. The hair can further be left with increased levels of static upon drying, which can interfere with combing and result in a condition commonly referred to as "fly-away hair."

A variety of approaches have been developed to alleviate these after-shampoo problems. These approaches range from post-shampoo application of hair conditioners such as leave-on and rinse-off products, to hair conditioning shampoos which attempt to both clean and condition the hair from a single product.

Cationic conditioning materials are useful in conditioning shampoos due to their conditioning benefits when the hair is dried. Coacervate formation in a shampoo composition is known to be advantageous for incorporating cationic conditioning agents to provide a stable product. The use of cationic conditoning agents to form coacervates are known in the art, such as in PCT publications WO93/08787 and WO95/01152.

However, incorporation of such cationic conditioning materials via coacervate formation alone is not capable of delivering satisfactory conditioning benefit when the hair is dried.

Based on the foregoing, there remains a need to provide a conditioning shampoo composition including cationic conditioning materials, which provides improved conditioning benefit when the hair is dried such as prevention of fly away, ease of combing, and soft and moist feeling.

None of the existing art provides all of the advantages and benefits of the present invention.

SUMMARY

The present invention is directed to a conditioning shampoo composition comprising by weight:

(a) from about 0.05% to about 50% of a polyhydrophilic anionic surfactant;

(b) from about 0.05% to about 20% of a cationic conditioning agent selected from the group consisting of cationic surfactants, cationic polymers, and mixtures thereof;

(c) from about 0.2% to about 20% of a cationic silicone emulsion comprising by weight of the cationic silicone emulsion from about 2% to about 20% of a cationic surfactant; and an emulsifiable amount of a silicone compound having a particle size of less than about 50 microns; and

(d) an aqueous carrier.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

DETAILED DESCRIPTION

While the specification concludes with claims which particularly point out and distinctly claim the invention, it is believed the present invention will be better understood from the following description.

All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

Herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

All percentages, parts and ratios are based upon the total weight of the compositions of the present invention, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include carriers or by-products that may be included in commercially available materials.

POLYHYDROPHILIC ANIONIC SURFACTANT

The present invention comprises by weight from about 0.05% to about 50%, preferably from about 0.1% to about 30%, more preferably from about 0.5% to about 20% of a polyhydrophilic anionic surfactant. Polyhydrophilic anionic surfactants useful herein are those having at least two anionic hydrophilic groups in the molecule. One molecule of a polyhydrophilic anionic surfactant may comprise the same hydrophilic groups, or different hydrophilic groups. Preferably, the hydrophilic group is selected from the group consisting of carboxy, sulfate, sulfonate, and phosphate groups, more preferably at least one carboxy group, still preferably at least two carboxy groups.

Without being bound by theory, it is believed that polyhydrophilic anionic surfactants herein, with the presence of cationic conditioning agents, are capable of providing a coacervate with a large region which can trap and deliver an increased amount of conditioning agents to the hair surface. It is also believed that coacervates made with polyhydrophilic anionic surfactants herein are readily separated from the water phase, thus also resulting in delivery of an increased amount of conditioning agents to the hair surface.

Nonlimiting examples of polyhydrophilic anionic surfactants include N-acyl-L-glutamates such as N-cocoyl-L-glutamate and, N-lauroyl-L-glutamate, sodium lauryl aminodiacetic acid, laurimino diproprionate, and N-lauryl-β-imino-dipropionate, N-acyl-L-aspartate, polyoxyethylene laurylsulfosuccinate, disodium N-octadecylsulfosuccinate; disodium lauryl sulfosuccinate; diammonium lauryl sulfosuccinate; tetra sodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinate; the diamyl ester of sodium sulfosuccinic acid; the dihexyl ester of sodium sulfosuccinic acid; and the dioctyl ester of sodium sulfosuccinic acid, and 2-cocoalkyl N-carboxyethyl N-carboxyethoxyethyl imidazolinium betaine.

Other suitable polyhydrophilic anionic surfactants include those of the following formula (I) and (II):

```
HO2CH2C-N-CH2CH2N(CH2COOH)2
        |
        C=O                              (I)
        |
        R
```

wherein R is an alkyl of 12 to 18 carbons; and

```
         O
         ||  /CH2CH2NCOOM1
  R'—C—N                              (II)
             \CH2CH2NCOOM2
```

wherein R' is a straight or branched alkyl or alkenyl of 5 to 21 carbons; and M1 and M2, independently, are hydrogen, alkaline metal, alkaline earth metal, ammonium, alkyl or alkenyl ammonium of 1 to 22 carbons, alkyl or alkenyl substituted pyridinium of 1 to 18 carbons, or basic amino acids. Suitable examples of formula (I) include acid salts of N-acyl-N,N'-ethylenediaminetriacetic acid, such as sodium, triethanolamine and ammonium salts of lauroyl-N,N'-ethylenediaminetriacetic acid, myristoyl-N,N'-ethylenediaminetriacetic acid, cocoyl-N,N'-ethylenediaminetriacetic acid, and oleoyl-N,N'-ethylenediaminetriacetic acid. Suitable examples of formula (II) include acid and salt forms of N-hexanoyl-N-carboxyethyl-β-alanine, N-octanoyl-N-carboxyethyl-β-alanine, N-decanoyl-N-carboxyethyl-β-alanine, N-lauroyl-N-carboxyethyl-β-alanine, N-tetradecanoyl-N-hydroxyethyl-β-alanine, N-hexadecanoyl-N-carboxyethyl-β-alanine, N-isostearoyl-N-carboxyethyl-β-alanine, and N-oleoyl-N-carboxyethyl-β-alanine.

Commercially available polyhydrophilic anionic surfactants suitable in the present invention are N-acyl-L-glutamate with a tradename AMISOFT CT-12S, N-cocoyl-L-glutamate with a tradename EMCOL 4400-1 supplied by Witco, lauroyl glutamate with a tradename AMISOFT LS-11, and acylaspartate with tradenames ASPARACK and AAS supplied by Mitsubishi Chemical, sodium lauryl aminodiacetic acid with a tradename NISSAN ANON LA supplied by Nippon Oil and Fat; and N-acyl-N,N'-ethylenediaminetriacetic acid derivaties with tradename ED3A supplied by Hampshire Chemical Corp.

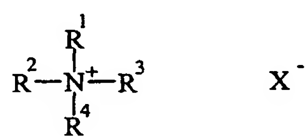
CATIONIC CONDITIONING AGENT

The present invention comprises by weight from about 0.05% to about 20% of a cationic conditioning agent. The cationic conditioning agents are selected from the group consisting of cationic surfactants, cationic polymers, and mixtures thereof.

Cationic Surfactant

The cationic surfactants useful herein are any known to the artisan.

Among the cationic surfactants useful herein are those corresponding to the general formula (I):



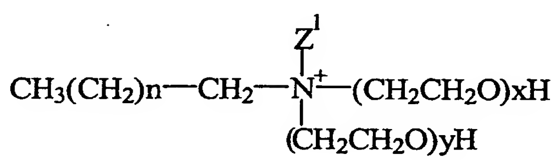
(I)

wherein at least one of R^1, R^2, R^3, and R^4 is selected from an aliphatic group of from 8 to 30 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms, the remainder of R^1, R^2, R^3, and R^4 are independently selected from an aliphatic group of from 1 to about 22 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate, nitrate, sulfonate, sulfate, alkylsulfate, and alkyl sulfonate radicals. The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated. Preferred is when R^1, R^2, R^3, and R^4 are independently selected from C_1 to about C_{22} alkyl. Nonlimiting examples of cationic surfactants useful in the present invention include the materials having the following CTFA designations: quaternium-8, quaternium-14, quaternium-18, quaternium-18 methosulfate, quaternium-24, and mixtures thereof.

Among the cationic surfactants of general formula (I), preferred are those containing in the molecule at least one alkyl chain having at least 16 carbons. Nonlimiting examples of such preferred cationic surfactants include: behenyl trimethyl ammonium chloride available, for example, with tradename INCROQUAT TMC-80 from Croda and ECONOL TM22 from Sanyo Kasei; cetyl

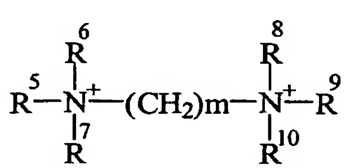
trimethyl ammonium chloride available, for example, with tradename CA-2350 from Nikko Chemicals, hydrogenated tallow alkyl trimethyl ammonium chloride, dialkyl (14-18) dimethyl ammonium chloride, ditallow alkyl dimethyl ammonium chloride, dihydrogenated tallow alkyl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, di(behenyl/arachidyl) dimethyl ammonium chloride, dibehenyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, stearyl propyleneglycol phosphate dimethyl ammonium chloride, stearoyl amidopropyl dimethyl benzyl ammonium chloride, stearoyl amidopropyl dimethyl (myristylacetate) ammonium chloride, and N-(stearoyl colamino formyl methy) pyridinium chloride.

Also preferred are hydrophilically substituted cationic surfactants in which at least one of the substituents contain one or more aromatic, ether, ester, amido, or amino moieties present as substituents or as linkages in the radical chain, wherein at least one of the R^1 - R^4 radicals contain one or more hydrophilic moieties selected from alkoxy (preferably C_1 - C_3 alkoxy), polyoxyalkylene (preferably C_1 - C_3 polyoxyalkylene), alkylamido, hydroxyalkyl, alkylester, and combinations thereof. Preferably, the hydrophilically substituted cationic conditioning surfactant contains from 2 to about 10 nonionic hydrophile moieties located within the above stated ranges. Preferred hydrophilically substituted cationic surfactants include those of the formula (II) through (VIII) below:



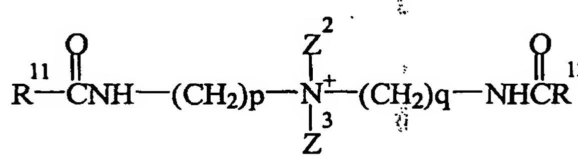
X^- (II)

wherein n is from 8 to about 28, x+y is from 2 to about 40, Z^1 is a short chain alkyl, preferably a $C_1 - C_3$ alkyl, more preferably methyl, or $(CH_2CH_2O)_zH$ wherein x+y+z is up to 60, and X is a salt forming anion as defined above;

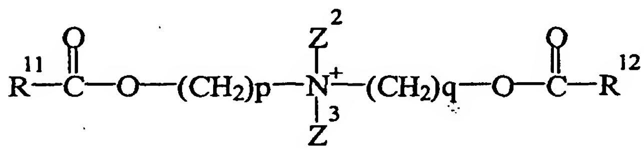


$2X^-$ (III)

wherein m is 1 to 5, one or more of R^5, R^6, and R^7 are independently an C_1 - C_{30} alkyl, the remainder are CH_2CH_2OH, one or two of R^8, R^9, and R^{10} are independently an C_1 - C_{30} alkyl, and remainder are CH_2CH_2OH, and X is a salt forming anion as mentioned above;

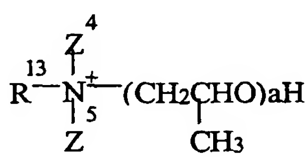


X^- (IV)



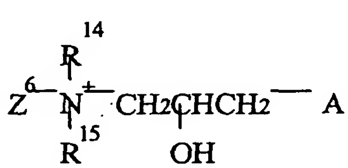
X^- (V)

wherein, independently for formulae (IV) and (V), Z^2 is an alkyl, preferably a C_1 - C_3 alkyl, more preferably methyl, and Z^3 is a short chain hydroxyalkyl, preferably hydroxymethyl or hydroxyethyl, p and q independently are integers from 2 to 4, inclusive, preferably from 2 to 3, inclusive, more preferably 2, R^{11} and R^{12}, independently, are substituted or unsubstituted hydrocarbyls, preferably C_{12} - C_{20} alkyl or alkenyl, and X is a salt forming anion as defined above;



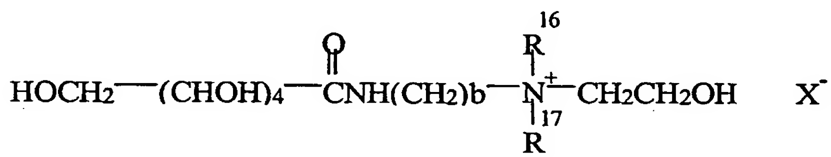
X^- , (VI)

wherein R^{13} is a hydrocarbyl, preferably a C_1 - C_3 alkyl, more preferably methyl, Z^4 and Z^5 are, independently, short chain hydrocarbyls, preferably C_2 - C_4 alkyl or alkenyl, more preferably ethyl, a is from 2 to about 40, preferably from about 7 to about 30, and X is a salt forming anion as defined above;



X^- (VII)

wherein R^{14} and R^{15}, independently, are C_1 - C_3 alkyl, preferably methyl, Z^6 is a C_{12} - C_{22} hydrocarbyl, alkyl carboxy or alkylamido, and A is a protein, preferably a collagen, keratin, milk protein, silk, soy protein, wheat protein, or hydrolyzed forms thereof; and X is a salt forming anion as defined above;



(VIII)

wherein b is 2 or 3, R^{16} and R^{17}, independently are C_1 - C_3 hydrocarbyls preferably methyl, and X is a salt forming anion as defined above. Nonlimiting examples of hydrophilically substituted cationic surfactants useful in the present invention include the materials having the following CTFA designations: quaternium-16, quaternium-26, quaternium-27, quaternium-30, quaternium-33, quaternium-43, quaternium-52, quaternium-53, quaternium-56, quaternium-60, quaternium-61, quaternium-62, quaternium-70, quaternium-71, quaternium-72, quaternium-75, quaternium-76 hydrolyzed collagen, quaternium-77, quaternium-78, quaternium-79 hydrolyzed collagen, quaternium-79 hydrolyzed keratin, quaternium-79 hydrolyzed milk protein, quaternium-79 hydrolyzed silk, quaternium-79 hydrolyzed soy protein, and quaternium-79 hydrolyzed wheat protein, quaternium-80, quaternium-81, quaternium-82, quaternium-83, quaternium-84, and mixtures thereof.

Highly preferred hydrophilically substituted cationic surfactants include dialkylamido ethyl hydroxyethylmonium salt, dialkylamidoethyl dimonium salt, dialkyloyl ethyl hydroxyethylmonium salt, dialkyloyl ethyldimonium salt, and mixtures thereof; for example, commerically available under the following tradenames; VARISOFT 110, VARIQUAT K1215 and 638 from Witco Chemical, MACKPRO KLP, MACKPRO WLW, MACKPRO MLP, MACKPRO NSP, MACKPRO NLW, MACKPRO WWP, MACKPRO NLP, MACKPRO SLP from McIntyre, ETHOQUAD 18/25, ETHOQUAD O/12PG, ETHOQUAD C/25, ETHOQUAD S/25, and ETHODUOQUAD from Akzo, DEHYQUAT SP from Henkel, and ATLAS G265 from ICI Americas.

Salts of primary, secondary, and tertiary fatty amines are also suitable cationic surfactants. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and can be substituted or unsubstituted.

Particularly useful are amido substituted tertiary fatty amines. Such amines, useful herein, include stearamidopropyldimethylamine, stearamidopropyldiethylamine, stearamidoethyldiethylamine, stearamidoethyldimethylamine, palmitamidopropyldimethylamine, palmitamidopropyldiethylamine, palmitamidoethyldiethylamine, palmitamidoethyldimethylamine, behenamidopropyldimethylamine, behenamidopropyldiethylamine, behenamidoethyldiethylamine, behenamidoethyldimethylamine, arachidamidopropyldimethylamine, arachidamidopropyldiethylamine, arachidamidoethyldiethylamine, arachidamidoethyldimethylamine, diethylaminoethylstearamide. Also useful are dimethylstearamine, dimethylsoyamine, soyamine, myristylamine, tridecylamine, ethylstearylamine, N-tallowpropane diamine, ethoxylated (with 5 moles of ethylene oxide) stearylamine, dihydroxyethylstearylamine, and arachidylbehenylamine. These amines can also be used in combination with acids such as L-glutamic acid, lactic acid, hydrochloric acid, malic acid, succinic acid, acetic acid, fumaric acid, tartaric acid, citric acid, L-glutamic hydrochloride, and mixtures thereof; more preferably L-glutamic acid, lactic acid, citric acid. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Patent 4,275,055, Nachtigal, et al., issued June 23, 1981, which is incorporated by reference herein in its entirety.

The cationic surfactants for use herein may also include a plurality of ammonium quaternary moieties or amino moieties, or a mixture thereof.

Cationic Polymers

The hair conditioning compositions of the present invention can further comprise one or more cationic polymer as a cationic conditioning agent. As used herein, the term "polymer" shall include materials whether made by polymerization of one type of monomer or made by two (i.e., copolymers) or more types of monomers.

Preferably, the cationic polymer is a water-soluble cationic polymer. By "water soluble" cationic polymer, what is meant is a polymer which is sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% in water (distilled or equivalent) at 25°C. The preferred polymer will be sufficiently soluble to form a substantially clear solution at 0.5% concentration, more preferably at 1.0% concentration.

The cationic polymers hereof will generally have a weight average molecular weight which is at least about 5,000, typically at least about 10,000, and is less than about 10 million. Preferably, the molecular weight is from about 100,000 to about 2 million. The cationic polymers will generally have cationic nitrogen-containing moieties such as quaternary ammonium or cationic amino moieties, and mixtures thereof.

The cationic charge density is preferably at least about 0.1 meq/gram, more preferably at least about 1.5 meq/gram, even more preferably at least about 1.1 meq/gram, still more preferably at least about 1.2 meq/gram. Cationic charge density of the cationic polymer can be determined according to the Kjeldahl Method. Those skilled in the art will recognize that the charge density of amino-containing polymers may vary depending upon pH and the isoelectric point of the amino groups. The charge density should be within the above limits at the pH of intended use.

Any anionic counterions can be utilized for the cationic polymers so long as the water solubility criteria is met. Suitable counterions include halides (e.g., Cl, Br, I, or F, preferably Cl, Br, or I), sulfate, and methylsulfate. Others can also be used, as this list is not exclusive.

The cationic nitrogen-containing moiety will be present generally as a substituent, on a fraction of the total monomer units of the cationic hair conditioning polymers. Thus, the cationic polymer can comprise copolymers, terpolymers, etc. of quaternary ammonium or cationic amine-substituted monomer units and other non-cationic units referred to herein as spacer monomer units. Such polymers are known in the art, and a variety can be found in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, edited by Estrin, Crosley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C., 1982).

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl methacrylate, vinyl caprolactone, and vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably have C_1 - C_7 alkyl groups, more preferably C_1 - C_3 alkyl groups. Other suitable spacer monomers include vinyl esters, vinyl

alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene glycol, and ethylene glycol.

The cationic amines can be primary, secondary, or tertiary amines, depending upon the particular species and the pH of the composition. In general, secondary and tertiary amines, especially tertiary amines, are preferred.

Amine-substituted vinyl monomers can be polymerized in the amine form, and then optionally can be converted to ammonium by a quaternization reaction. Amines can also be similarly quaternized subsequent to formation of the polymer. For example, tertiary amine functionalities can be quaternized by reaction with a salt of the formula R'X wherein R' is a short chain alkyl, preferably a C_1 - C_7 alkyl, more preferably a C_1 - C_3 alkyl, and X is an anion which forms a water soluble salt with the quaternized ammonium.

Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidone, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidone salts. The alkyl portions of these monomers are preferably lower alkyls such as the C_1 - C_3 alkyls, more preferably C_1 and C_2 alkyls. Suitable amine-substituted vinyl monomers for use herein include dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylamide, and dialkylaminoalkyl methacrylamide, wherein the alkyl groups are preferably C_1 - C_7 hydrocarbyls, more preferably C_1 - C_3, alkyls.

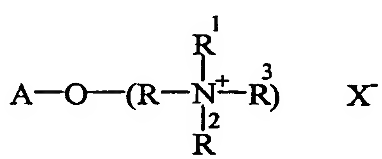
The cationic polymers hereof can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic hair conditioning polymers include, for example: copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (e.g., chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA", as Polyquaternium-16), such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-

pyrrolidone and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11) such as those commercially available from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N); cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral acid salts of amino-alkyl esters of homo- and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256, incorporated herein by reference.

Other cationic polymers that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives.

Cationic polysaccharide polymer materials suitable for use herein include those of the formula:



wherein: A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual, R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof, R^1, R^2, and R^3 independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R^1, R^2 and R^3) preferably being about 20 or less, and X is an anionic counterion, as previously described.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR® and LR® series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200®.

Other cationic polymers that can be used include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride (commercially available from Celanese Corp. in their Jaguar R series). Other materials include quaternary nitrogen-containing cellulose ethers (e.g., as described in U.S. Patent 3,962,418, incorporated herein by reference), and copolymers of etherified cellulose and starch (e.g., as described in U.S. Patent 3,958,581, incorporated herein by reference.)

CATIONIC SILICONE EMULSION

The compositions of the present invention comprise from about 0.2% to about 20%, preferably from about 1% to about 10%, and more preferably from about 0.5% to about 5% of a cationic silicone emulsion. The cationic silicone emulsion herein is a pre-dispersed stable emulsion comprising at least a cationic surfactant, a silicone particle, and water. The cationic silicone emulsion comprises, by weight of the cationic silicone emulsion, from about 2% to about 20%, preferably from about 2% to about 8%, of a cationic surfactant; and an emulsifiable amount of silicone compound. The silicone compound is preferably comprised from about 0.1% to about 70%, more preferably from about 5% to about 60% by weight of the cationic silicone emulsion. The amount of silicone compound to the entire composition is preferably from about 0.1% to about 10% by weight.

The cationic silicone emulsion can be made in any convenient method known in the art.

For example, the cationic silicone emulsion may be made by mechanical emulsification by taking a polysiloxane polymer and emulsifying it in water in the presence of at least one emulsifying agent using mechanical means such as agitation, shaking and homogenization. The emulsifying agent can be the cationic surfactant comprised in the cationic silicone emulsion, or other suitable surfactant. Mechanical emulsification may require use of two or more surfactants, and two or more mixing processes using different surfactants. Two or more types of silicone compounds, such as a highly viscous silicone compound and a low viscosity silicone compound, may be used. One particularly preferred process for obtaining the cationic silicone emulsion of the present invention via mechanical emulsification is through the process disclosed in EP Publication 460,683A, which is incorporated herein by reference in its entirety. In this reference, it is disclosed that the emulsion is prepared by combining the

polysiloxane, water, and a primary nonionic surfactant having an HLB value of 15-19 to form a first mixture, adding to the first mixture a co-surfactant selected from the group consisting of nonionic, cationic and anionic surfactants having an HLB value of 1.8-15 to form a second mixture and mixing the second mixture at a temperature of about 40°C, until the particle size of the polysiloxane in the emulsion is less than about three hundred nanometers.

The cationic silicone emulsion herein may be made by emulsion polymerization. An emulsion polymerization process includes taking a polysiloxane monomer and/or oligomer and emulsifying it in water in the presence of a catalyst to form the polysiloxane polymer. It is understood that unreacted monomers and oligomers may remain in an emulsion polymerized silicone emulsion. One particularly preferred process for obtaining the cationic silicone emulsion of the present invention via emulsion polymerization is through the process disclosed in GB application 2,303,857, which is incorporated herein by reference in its entirety. This reference discloses a process for making stable cationic silicone oil-in-water emulsion comprising: 1) blending a mixture of silicones selected from the group consisting of cyclic silicone oligomers, mixed silicone hydrolyzates, silanol stopped oligomers, high molecular weight silicone polymers, and functionalized silicones with 2) water, and 3) an anionic surfactant; 4) heating the blend to a temperature ranging from about 75 to about 98°C for a period of time ranging from about 1 hours to about 5 hours; 5) cooling the heated blend to a temperature ranging from 0 to about 25°C for a period of time ranging from about 3 hours to about 24 hours; 6) adding a compatibilizing surfactant selected from the group consisting of nonionic surfactant having an HLB ratio greater than 9; and 7) adding a cationic surfactant.

It is of particular significance that the cationic surfactants mentioned here are present in the cationic silicone emulsion, and not the bulk of the composition. It has been found that products having cationic surfactants in the cationic silicone emulsion provide improvement to the dry hair feel significantly more than products having cationic surfactants in the bulk of the composition.

The silicone compound in the cationic silicone emulsion have a particle size of less than about 50 microns, preferably from about 0.2 to about 2.5 microns, more preferably from about 0.2 to about 0.5 microns. The particle size of the silicone compound is believed to affect the deposition of the silicone compound on the hair. The particle size of the silicone compound is determined

based on the desired deposition and uniformity of distribution of the silicone compound.

In a particularly preferred embodiment, the cationic silicone emulsion comprises from about 2% to about 8% cationic surfactant, from about 10% to about 70% silicone compound, and the remainder water and other emulsifying surfactants. In another particularly preferred embodiment, the cationic silicone emulsion comprises from about 4% to about 8% cationic surfactant, from about 10% to about 70% silicone compound, and the remainder water and other emulsifying surfactants.

Cationic Surfactants

The cationic surfactant comprised in the cationic silicone emulsion is selected from the species disclosed above under the title "Cationic Surfactant".

Silicone Compounds

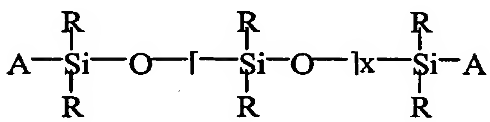
The cationic silicone emulsion herein comprises silicone compounds in an amount capable of providing a stable emulsion, preferably from about 0.1% to about 70%, more preferably from about 5% to about 60% by weight of the cationic silicone emulsion. The amount of silicone compound to the entire composition is preferably from about 0.1% to about 10% by weight. The silicone compounds hereof can include volatile soluble or insoluble, or nonvolatile soluble or insoluble silicone conditioning agents. By soluble what is meant is that the silicone compound is miscible with the carrier of the composition so as to form part of the same phase. By insoluble what is meant is that the silicone forms a separate, discontinuous phase from the carrier, such as in the form of an emulsion or a suspension of droplets of the silicone. The silicone compounds herein may be made by conventional polymerization, or emulsion polymerization.

The silicone compounds for use herein will preferably have a viscosity of from about 1,000 to about 2,000,000 centistokes at 25^{O}C, more preferably from about 10,000 to about 1,800,000, and even more preferably from about 25,000 to about 1,500,000. The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970, which is incorporated by reference herein in its entirety. Silicone compound of high molecular weight may be made by emulsion polymerization.

Silicone compounds useful herein include polyalkyl polyaryl siloxanes, polyalkyleneoxide-modified siloxanes, silicone resins, amino-substituted siloxanes, and mixtures thereof. The silicone compound is preferably selected

from the group consisting of polyalkyl polyaryl siloxanes, polyalkyleneoxide-modified siloxanes, silicone resins, and mixtures thereof, and more preferably from one or more polyalkyl polyaryl siloxanes.

Polyalkyl polyaryl siloxanes useful here in include those with the following structure (I)



(I)

wherein R is alkyl or aryl, and x is an integer from about 7 to about 8,000. "A" represents groups which block the ends of the silicone chains. The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) can have any structure as long as the resulting silicone remains fluid at room temperature, is dispersible, is neither irritating, toxic nor otherwise harmful when applied to the hair, is compatible with the other components of the composition, is chemically stable under normal use and storage conditions, and is capable of being deposited on and conditions the hair. Suitable A groups include hydroxy, methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicon atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicone compounds are polydimethylsiloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane, which is also known as dimethicone, is especially preferred. The polyalkylsiloxanes that can be used include, for example, polydimethylsiloxanes. These silicone compounds are available, for example, from the General Electric Company in their ViscasilR and SF 96 series, and from Dow Corning in their Dow Corning 200 series. Polymethylphenylsiloxanes, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid, are useful herein.

Also preferred, for enhancing the shine characteristics of hair, are highly arylated silicone compounds, such as highly phenylated polyethyl silicone having refractive index of about 1.46 or higher, especially about 1.52 or higher. When these high refractive index silicone compounds are used, they should be mixed with a spreading agent, such as a surfactant or a silicone resin, as described

below to decrease the surface tension and enhance the film forming ability of the material.

Another polyalkyl polyaryl siloxane that can be especially useful is a silicone gum. The term "silicone gum", as used herein, means a polyorganosiloxane material having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. It is recognized that the silicone gums described herein can also have some overlap with the above-disclosed silicone compounds. This overlap is not intended as a limitation on any of these materials. Silicone gums are described by Petrarch, and others including U.S. Patent No. 4,152,416, to Spitzer et al., issued May 1, 1979 and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. All of these described references are incorporated herein by reference in their entirety. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include polydimethylsiloxane, poly(dimethylsiloxane methylvinylsiloxane) copolymer, poly(dimethylsiloxane diphenylsiloxane methylvinylsiloxane) copolymer and mixtures thereof.

Polyalkyleneoxide-modified siloxanes useful herein include, for example, polypropylene oxide modified and polyethylene oxide modified polydimethylsiloxane. The ethylene oxide and polypropylene oxide level should be sufficiently low so as not to interfere with the dispersibility characteristics of the silicone. These material are also known as dimethicone copolyols.

Silicone resins, which are highly crosslinked polymeric siloxane systems, are useful herein. The crosslinking is introduced through the incorporation of tri-functional and tetra-functional silanes with mono-functional or di-functional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units, and hence, a sufficient level of crosslinking, such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone

resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinylchlorosilanes, and tetrachlorosilane, with the methyl substituted silanes being most commonly utilized. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art. Without being bound by theory, it is believed that the silicone resins can enhance deposition of other silicone compounds on the hair and can enhance the glossiness of hair with high refractive index volumes.

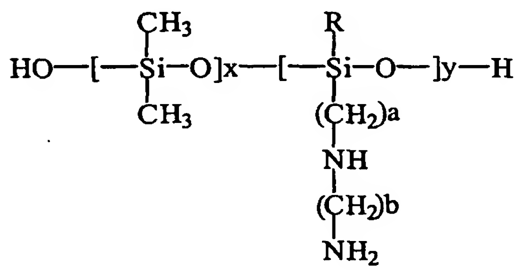
Other useful silicone resins are silicone resin powders such as the material given the CTFA designation polymethylsilsequioxane, which is commercially available as Tospearl™ from Toshiba Silicones.

Silicone resins can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as the "MDTQ" nomenclature. Under this system, the silicone is described according to the presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the mono-functional unit $(CH_3)_3SiO)_{.5}$; D denotes the difunctional unit $(CH_3)_2SiO$; T denotes the trifunctional unit $(CH_3)SiO_{1.5}$; and Q denotes the quadri- or tetra-functional unit SiO_2. Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyl, amino, hydroxyl, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone, or an average thereof, or as specifically indicated ratios in combination with molecular weight, complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MQ and MDTQ resins. Thus, the preferred silicone substituent is methyl.

Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

Amino-substituted siloxanes useful herein include those represented by the following structure (II)



(II)

wherein R is CH_3 or OH, x and y are integers which depend on the molecular weight, the average molecular weight being approximately between 5,000 and 10,000. This polymer is also known as "amodimethicone".

Suitable amino-substituted siloxane fluids include those represented by the formula (III)

$$(R_1)_aG_{3-a}\text{-Si-}(\text{-OSiG}_2)_n\text{-}(\text{-OSiG}_b(R_1)_{2-b})_m\text{-O-SiG}_{3-a}(R_1)_a \qquad \text{(III)}$$

in which G is chosen from the group consisting of hydrogen, phenyl, OH, C_1-C_8 alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0; b denotes 0 or 1 and preferably equals 1; the sum n+m is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R_1 is a monovalent radical of formula $C_qH_{2q}L$ in which q is an integer from 2 to 8 and L is chosen from the groups

$-N(R_2)CH_2-CH_2-N(R_2)_2$

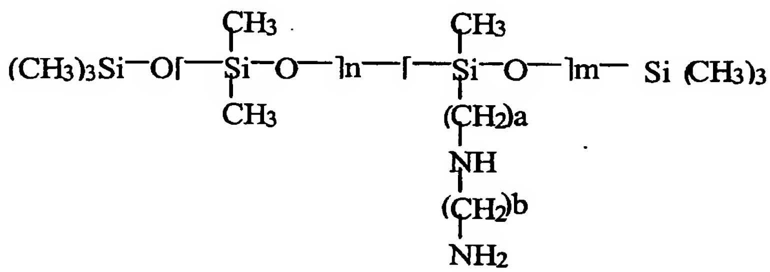
$-N(R_2)_2$

$-N(R_2)_3A^-$

$-N(R_2)CH_2-CH_2-NR_2H_2A^-$

in which R_2 is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and A^- denotes a halide ion.

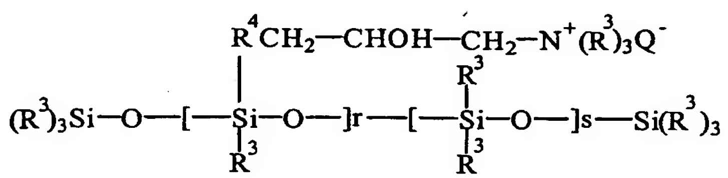
An especially preferred amino-substituted siloxane corresponding to formula (III) is the polymer known as "trimethylsilylamodimethicone", of formula (IV):



(IV)

In this formula n and m are selected depending on the molecular weight of the compound desired.

Other amino-substituted siloxane which can be used are represented by the formula (V):



(V)

where R^3 denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl; R_4 denotes a hydrocarbon radical, preferably a $C_1 - C_{18}$ alkylene radical or a $C_1 - C_{18}$, and more preferably $C_1 - C_8$, alkyleneoxy radical; Q^- is a halide ion, preferably chloride; r denotes an average statistical value from 2 to 20, preferably from 2 to 8; s denotes an average statistical value from 20 to 200, and preferably from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCAR SILICONE ALE 56."

<u>AQUEOUS CARRIER</u>

The compositions of the present invention comprise an aqueous carrier. The level and species of the carrier are selected according to the compatibility with other components, and other desired characteristic of the product.

The carrier useful in the present invention include water and water solutions of lower alkyl alcohols and polyhydric alcohols. The lower alkyl alcohol useful herein are monohydric alcohols having 1 to 6 carbons, more preferably

ethanol and isopropanol. The polyhydric alcohols useful herein include propylene glycol, hexylene glycol, glycerin, and propane diol.

Preferably, the aqueous carrier is substantially water. Deionized water is preferably used. Water from natural sources including mineral cations can also be used, depending on the desired characteristic of the product. Generally, the compositions of the present invention comprise from about 20% to about 95%, preferably from about 30% to about 92%, and more preferably from about 50% to about 90% water.

ADDITIONAL DETERSIVE SURFACTANT

The compositions of the present invention may further contain an additional detersive surfactant selected from the group consisting of secondary anionic surfactants, amphoteric surfactants, zwitterionic surfactants, nonionic surfactants, and mixtures thereof. The level and species of the additional detersive surfactant are selected according to the compatibility with other components, and desired characteristic of the product.

In preferred embodiments, the additional detersive surfactant contains a secondary anionic surfactant, more preferably further contains an amphoteric surfactant.

The term detersive surfactant, as used herein, is intended to distinguish these surfactants from surfactants which are primarily emulsifying surfactants, i.e. surfactants which provide an emulsifying benefit and which have low cleansing performance. It is recognized that most surfactants have both detersive and emulsifying properties. It is not intended to exclude emulsifying surfactants from the present invention, provided the surfactant also possesses sufficient detersive properties to be useful herein.

When present, the additional detersive surfactant is included at a level so that the total of additional detersive surfactant and polyhydrophilic anionic surfactant are from about 5% to about 75%, preferably from about 8% to about 50%, and more preferably from about 10% to about 30%, by weight of the composition.

Secondary Anionic Surfactants

Anionic surfactants useful herein include alkyl and alkyl ether sulfates. These materials have the respective formulae $ROSO_3M$ and $RO(C_2H_4O)_xSO_3M$, wherein R is alkyl or alkenyl of from about 8 to about 30 carbon atoms, x is 1 to about 10, and M is hydrogen or a cation such as

ammonium, alkanolammonium (e.g., triethanolammonium), a monovalent metal cation (e.g., sodium and potassium), or a polyvalent metal cation (e.g., magnesium and calcium). Preferably, M should be chosen such that the anionic surfactant component is water soluble. The anionic surfactant or surfactants should be chosen such that the Krafft temperature is about 15°C or less, preferably about 10°C or less, and more preferably about 0°C or less. It is also preferred that the anionic surfactant be soluble in the composition hereof.

Krafft temperature refers to the point at which solubility of an ionic surfactant becomes determined by crystal lattice energy and heat of hydration, and corresponds to a point at which solubility undergoes a sharp, discontinuous increase with increasing temperature. Each type of surfactant will have its own characteristic Krafft temperature. Krafft temperature for ionic surfactants is, in general, well known and understood in the art. See, for example, Myers, Drew, Surfactant Science and Technology, pp. 82-85, VCH Publishers, Inc. (New York, New York, USA), 1988 (ISBN 0-89573-399-0), which is incorporated by reference herein in its entirety.

In the alkyl and alkyl ether sulfates described above, preferably R has from about 12 to about 18 carbon atoms in both the alkyl and alkyl ether sulfates. The alkyl ether sulfates are typically made as condensation products of ethylene oxide and monohydric alcohols having from about 8 to about 24 carbon atoms. The alcohols can be derived from fats, e.g., coconut oil, palm oil, tallow, or the like, or the alcohols can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil and palm oil are preferred herein. Such alcohols are reacted with 1 to about 10, and especially about 3, molar proportions of ethylene oxide and the resulting mixture of molecular species having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific examples of alkyl ether sulfates which can be used in the present invention are sodium and ammonium salts of coconut alkyl triethylene glycol ether sulfate; tallow alkyl triethylene glycol ether sulfate, and tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from about 12 to about 16 carbon atoms and an average degree of ethoxylation of from 1 to about 4 moles of ethylene oxide. Such a mixture also comprises from 0% to about 20% by weight C_{12-13} compounds;

from about 60% to about 100% by weight of $C_{14-15-16}$ compounds, from 0% to about 20% by weight of $C_{17-18-19}$ compounds; from about 3% to about 30% by weight of compounds having a degree of ethoxylation of 0; from about 45% to about 90% by weight of compounds having a degree of ethoxylation of from 1 to about 4; from about 10% to about 25% by weight of compounds having a degree of ethoxylation of from about 4 to about 8; and from about 0.1% to about 15% by weight of compounds having a degree of ethoxylation greater than about 8.

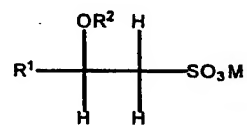
Other suitable anionic surfactants are the water-soluble salts of organic, sulfuric acid reaction products of the general formula $[R^1\text{-}SO_3\text{-}M]$ where R^1 is selected from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 10 to about 18, carbon atoms; and M is as previously described above in this section. Examples of such surfactants are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g., SO_3, H_2SO_4, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C_{10-18} n-paraffins.

Other anionic surfactants include olefin sulfonates having about 10 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of alpha-olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO_2, chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO_2, etc., when used in the gaseous form. The α-olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably about 14 to about 16 carbon atoms. Preferably, they are straight chain olefins. In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process. A

specific α-olefin sulfonate mixture of the above type is described more fully in U.S. Patent 3,332,880, to Pflaumer and Kessler, issued July 25, 1967, which is incorporated by reference herein in its entirety.

Still other suitable anionic surfactants are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut or palm oil; or sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other similar anionic surfactants are described in U.S. Patents 2,486,921, 2,486,922, and 2,396,278, which are incorporated by reference herein in their entirety.

Another class of anionic surfactants suitable for use in the shampoo compositions are the β-alkyloxy alkane sulfonates. These compounds have the following formula:



where R^1 is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R^2 is a lower alkyl group having from about 1, preferred, to about 3 carbon atoms, and M is as hereinbefore described. Many other anionic surfactants suitable for use in the shampoo compositions are described in McCutcheon's, Emulsifiers and Detergents, 1989 Annual, published by M. C. Publishing Co., and in U.S. Patent 3,929,678, which descriptions are incorporated herein by reference in their entirety.

Another class of suitable anionic surfactants are amino acid surfactants which are sufactants that have the basic chemical structure of an amino acid compound, i.e., that contains a structural component of one of the naturally-occurring amino acids.

Preferred anionic surfactants for use in the shampoo compositions include ammonium laureth sulfate, triethylamine laureth sulfate, triethanolamine laureth sulfate, monoethanolamine laureth sulfate, diethanolamine laureth sulfate, lauric monoglyceride sodium sulfate, sodium laureth sulfate, potassium laureth sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate, N-cocoylalaninate, N-acyl-N-methyl-β-alaninate, sodium laurylsarcosinate, cocoyl sarcosine, lauroyl taurate, lauroyl lactylate, N-acyl potassium glysine,

lauroamphohydroxy propylsulfonate, cocoglyceride sulfate, lauroyl isethionate, lauroamphoacetate, and mixtures thereof.

Amphoteric Surfactants

Amphoteric surfactants useful herein include those called zwitterionic surfactants in the art. Amphoteric surfactants useful herein include the derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical is straight or branched and one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate.

Amphoteric surfactants for use herein include the derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals are straight or branched, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:

$$\begin{array}{c} \quad (R^3)_x \\ \quad | \\ R^2 - Y^+ - CH_2 - R^4 - Z^- \end{array}$$

where R^2 contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R^3 is an alkyl or monohydroxyalkyl group containing 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R^4 is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples of amphoteric surfactants also include sultaines and amidosultaines. Sultaines, including amidosultaines, include for example, cocodimethylpropylsultaine, stearyldimethylpropylsultaine, lauryl-bis-(2-hydroxyethyl)propylsultaine and the like; and the amidosultaines such as cocamidodimethylpropylsultaine, stearylamidododimethylpropylsultaine, laurylamido-bis-(2-hydroxyethyl)propylsultaine, and the like. Preferred are amidohydroxysultaines such as the C_8–C_{18} hydrocarbylamidopropylhydroxy

sultaines, especially C_8–C_{14} hydrocarbylamidopropylhydroxysultaines, e.g., laurylamidopropylhydroxysultaine and cocamidopropylhydroxysultaine. Other sultaines are described in U.S. Patent 3,950,417, which is incorporated herein by reference in its entirety.

Other suitable amphoteric surfactants are the aminoalkanoates of the formula $RNH(CH_2)_nCOOM$, the iminodialkanoates of the formula $RN[(CH_2)_mCOOM]_2$ and mixtures thereof; wherein n and m are numbers from 1 to about 4, R is C_8 - C_{22} alkyl or alkenyl, and M is hydrogen, alkali metal, alkaline earth metal, ammonium or alkanolammonium.

Other suitable amphoteric surfactants include those represented by the formula :

$$\begin{array}{ccccc} & & & R^3 & \\ & & & | & \\ R^1CON & - & (CH_2)_n & - N^+ - & CH_2Z \\ | & & & | & \\ R^4 & & & R^2 & \end{array}$$

wherein R^1 is C_8 - C_{22} alkyl or alkenyl, preferably C_8 - C_{16}, R^2 and R^3 is independently selected from the group consisting of hydrogen, $-CH_2CO_2M$, $-CH_2CH_2OH$, $-CH_2CH_2OCH_2CH_2COOM$, or $-(CH_2CH_2O)_mH$ wherein m is an integer from 1 to about 25, and R^4 is hydrogen, $-CH_2CH_2OH$, or $CH_2CH_2OCH_2CH_2COOM$, Z is CO_2M or CH_2CO_2M, n is 2 or 3, preferably 2, M is hydrogen or a cation, such as alkali metal (e.g., lithium, sodium, potassium), alkaline earth metal (beryllium, magnesium, calcium, strontium, barium), or ammonium. This type of surfactant is sometimes classified as an imidazoline-type amphoteric surfactant, although it should be recognized that it does not necessarily have to be derived, directly or indirectly, through an imidazoline intermediate. Suitable materials of this type are marketed under the tradename MIRANOL and are understood to comprise a complex mixture of species, and can exist in protonated and non-protonated species depending upon pH with respect to species that can have a hydrogen at R^2. All such variations and species are meant to be encompassed by the above formula.

Examples of surfactants of the above formula are monocarboxylates and di-carboxylates. Examples of these materials include

cocoamphocarboxypropionate, cocoamphocarboxypropionic acid, cocoamphocarboxyglycinate (alternately referred to as cocoamphodiacetate), and cocoamphoacetate.

Commercial amphoteric surfactants include those sold under the trade names MIRANOL C2M CONC. N.P., MIRANOL C2M CONC. O.P., MIRANOL C2M SF, MIRANOL CM SPECIAL (Miranol, Inc.); ALKATERIC 2CIB (Alkaril Chemicals); AMPHOTERGE W-2 (Lonza, Inc.); MONATERIC CDX-38, MONATERIC CSH-32 (Mona Industries); REWOTERIC AM-2C (Rewo Chemical Group); and SCHERCOTERIC MS-2 (Scher Chemicals).

Betaine surfactants suitable for use herein are those represented by the formula:

$$R^5\text{—}[\overset{\overset{\large O}{||}}{C}\text{—}\overset{\overset{\large R^4}{|}}{N}\text{—}(CH_2)_m]_n\text{—}\underset{\underset{\large R^3}{|}}{\overset{\overset{\large R^2}{|}}{N^+}}\text{—}Y\text{—}R^1$$

wherein: R^1 is a member selected from the group consisting of

COOM and $CH(OH)CH_2SO_3M$

R^2 is lower alkyl or hydroxyalkyl; R^3 is lower alkyl or hydroxyalkyl; R^4 is a member selected from the group consisting of hydrogen and lower alkyl; R^5 is higher alkyl or alkenyl; Y is lower alkyl, preferably methyl; m is an integer from 2 to 7, preferably from 2 to 3; n is the integer 1 or 0; M is hydrogen or a cation, as previously described, such as an alkali metal, alkaline earth metal, or ammonium. The term "lower alkyl" or "hydroxyalkyl" means straight or branch chained, saturated, aliphatic hydrocarbon radicals and substituted hydrocarbon radicals having from one to about three carbon atoms such as, for example, methyl, ethyl, propyl, isopropyl, hydroxypropyl, hydroxyethyl, and the like. The term "higher alkyl or alkenyl" means straight or branch chained saturated (i.e., "higher alkyl") and unsaturated (i.e., "higher alkenyl") aliphatic hydrocarbon radicals having from about 8 to about 20 carbon atoms such as, for example, lauryl, cetyl, stearyl, oleyl, and the like. It should be understood that the term "higher alkyl or alkenyl" includes mixtures of radicals which may contain one or more intermediate linkages such as ether or polyether linkages or non-functional substituents such

as hydroxyl or halogen radicals wherein the radical remains of hydrophobic character.

Examples of surfactant betaines of the above formula wherein n is zero which are useful herein include the alkylbetaines such as cocodimethylcarboxymethylbetaine, lauryldimethylcarboxymethylbetaine, lauryldimethyl-α-carboxyethylbetaine, cetyldimethylcarboxymethylbetaine, lauryl-bis-(2-hydroxyethyl)-carboxymethylbetaine, stearyl-bis-(2-hydroxypropyl)carboxymethylbetaine, oleyldimethyl-γ-carboxypropylbetaine, lauryl-bis-(2-hydroxypropyl)-α-carboxyethylbetaine, etc. The sulfobetaines may be represented by cocodimethylsulfopropylbetaine, stearyldimethylsulfopropylbetaine, lauryl-bis-(2-hydroxyethyl)-sulfopropylbetaine, and the like.

Specific examples of amido betaines and amidosulfobetaines useful herein include the amidocarboxybetaines, such as cocamidodimethylcarboxymethylbetaine, laurylamidodimethylcarboxymethylbetaine, cetylamidodimethylcarboxymethylbetaine, laurylamido-bis-(2-hydroxyethyl)-carboxymethylbetaine, cocamido-bis-(2-hydroxyethyl)-carboxymethylbetaine, etc. The amidosulfobetaines may be represented by cocamidodimethylsulfopropylbetaine, stearylamidodimethylsulfopropylbetaine, laurylamido-bis-(2-hydroxyethyl)-sulfopropylbetaine, and the like.

<u>Nonionic Surfactants</u>

The shampoo compositions of the present invention can comprise a nonionic surfactant. Nonionic surfactants include those compounds produced by condensation of alkylene oxide groups, hydrophilic in nature, with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature.

Preferred nonlimiting examples of nonionic surfactants for use in the shampoo compositions include the following:

(1) polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 20 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 10 to about 60 moles of ethylene oxide per mole of alkyl phenol;

(2) those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products;

(3) condensation products of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configurations, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms;

(4) long chain tertiary amine oxides of the formula [$R^1R^2R^3N \rightarrow O$] where R^1 contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and R^2 and R^3 contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals;

(5) long chain tertiary phosphine oxides of the formula [$RR'R''P \rightarrow O$] where R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moieties and R' and R" are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms;

(6) long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moieties;

(7) alkyl polysaccharide (APS) surfactants (e.g. alkyl polyglycosides), examples of which are described in U.S. Patent 4,565,647, which is incorporated herein by reference in its entirety, and which discloses APS surfactants having a hydrophobic group with about 6 to about 30 carbon atoms and a polysaccharide (e.g., polyglycoside) as the hydrophilic group; optionally, there can be a polyalkylene-oxide group joining the hydrophobic and hydrophilic moieties; and the alkyl group (i.e., the hydrophobic moiety) can be saturated or unsaturated, branched or unbranched, and unsubstituted or substituted (e.g., with hydroxy or cyclic rings); a preferred material is alkyl polyglucoside which is commercially available from Henkel, ICI Americas, and Seppic; and

(8) polyoxyethylene alkyl ethers such as those of the formula $RO(CH_2CH_2)_nH$ and polyethylene glycol (PEG) glyceryl fatty esters, such as

those of the formula $R(O)OCH_2CH(OH)CH_2(OCH_2CH_2)_nOH$, wherein n is from 1 to about 200, preferably from about 20 to about 100, and R is an alkyl having from about 8 to about 22 carbon atoms.

ADDITIONAL CONDITIONING AGENTS

The compositions of the present invention may further comprise from about 0.05% to about 20%, preferably from about 0.1% to about 10%, and more preferably from about 0.5% to about 10% of additional conditioning agents selected from the group consisting of betaine conditioning agents, amphoteric polymers, poly α-olefin oil, high melting point compounds, oily compounds, and nonionic polymers.

Betaine Conditioning Agent

Betaine conditioning agents useful herein are those which are capable of depositing on the hair and providing conditioning benefits. Although betaine conditioning agents herein may have some surfactant properties, they are generally too low to provide good cleaning properties. Betaine conditioning agents are preferably contained at a level of from about 0.2% to about 10%.

Betaine conditioning agents useful herein are those having general formulae (1) and (2), preferably (1):

$$R^5-[\overset{\overset{\large O}{\|}}{C}-\overset{\overset{\large R^4}{|}}{N}-(CH_2)_m]_n-\underset{\underset{\large R^3}{|}}{\overset{\overset{\large R^2}{|}}{N^+}}-Y-R^1 \qquad (1)$$

wherein: R^1 is COOM or $CH(OH)CH_2SO_3M$, preferably COOM; R^2 and R^3, independently, are hydrogen, alkyl of 1 to about 4 carbons, CH_2COOM, CH_2CH_2OH, $CH_2CH_2OCH_2CH_2COOM$, or $(CH_2CH_2O)_xH$ wherein x is an integer from 1 to about 25, preferably methyl or ethyl; R^4 is hydrogen or alkyl of 1 to about 4 carbons, preferably hydrogen; R^5 is a straight or branched, saturated or unsaturated alkyl of about 16 to about 30 carbon atoms, preferably a straight saturated or unsaturated alkyl of about 16 to about 22 carbon atoms; Y is an alkyl of 1 to about 4 carbons, preferably methyl; m is an integer from 1 to about 7, preferably from 1 to about 4; n is 1 or 0; and M is hydrogen or an alkali metal, alkaline earth metal, or ammonium; and

$$\begin{array}{c} (R^7)_p \\ | \\ R^6 - Y^+ - CH_2 - R^8 - Z - M \end{array} \qquad (2)$$

wherein R^6 is a saturated or unsaturated alkyl, alkenyl, or hydroxy alkyl of from about 16 to about 30 carbon atoms, preferably a saturated or unsaturated alkyl of about 16 to about 22 carbon atoms; Y is nitrogen, phosphorus or sulfur atom; R^7 is an alkyl or monohydroxyalkyl group containing 1 to about 4 carbon atoms; p is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R^8 is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms; Z is a carboxylate, sulfonate, sulfate, phosphonate, or phosphate; and M is as previously defined.

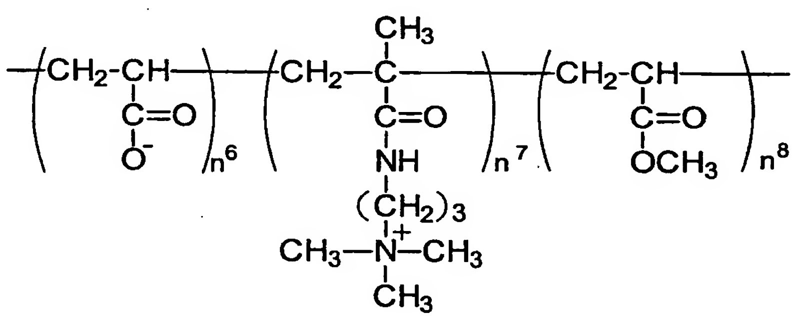
Examples of betaine conditioning agents useful herein include: alkylbetaines such as cetyldimethylcarboxymethylbetaine, stearyldimethylcarboxymethylbetaine, isostearyldimethylcarboxymethylbetaine, behenyldimethylcarboxymethylbetaine, oleyldimethylcarboxymethylbetaine, stearyl-bis-(2-hydroxypropyl) carboxymethylbetaine, oleyldimethyl-γ-carboxypropylbetaine, and stearyldihydroxyethylbetaine; amido betaines such as cetylamidodimethylcarboxymethyl betaine, isostearamidopropyl betaine, isostearylamidodimethylcarboxymethyl betaine, and stearylamidodimethylcarboxypropyl betaine; amidosulfobetaines such as stearylamidodimethylsulfopropylbetaine; sulfobetaines such as stearyldimethylsulfopropylbetaine; sultaines such as stearyldimethylpropylsultaine; and amidosultaines. Commercially available material highly suitable for use herein include stearyl dimethyl betaine with tradename Rikabion A-700 available from New Japan Chemical, oleyl dimethyl betaine with tradename Rikabion A-300 available from New Japan Chemical, and stearyl dihydroxyethyl betaine with tradename Anon AB 202 available from Nihon Oil & Fats.

<u>Amphoteric polymer</u>

The amphoteric polymers useful herein are those which provide conditioning benefit to the hair. Although some of the amphoteric polymers herein may have some hair holding or hair fixative properties, such hair holding or hair fixative properties are not a requirement for the amphoteric polymers herein. The amphoteric polymers useful herein are those including at least one

cationic monomer and at least one anionic monomer; the cationic monomer being quaternary ammonium, preferably dialkyl diallyl ammonium chloride or carboxylamidoalkyl trialkyl ammonium chloride; and the anionic monomer being carboxylic acid. The amphoteric polymers herein may include nonionic monomers such as acrylamine, methacrylate, or ethacrylate. Further, the amphoteric polymers useful herein do not contain betanized monomers. Amphoteric polymers are preferably contained at a level of from about 0.01% to about 5%.

Useful herein are polymers with the CTFA name Polyquaternium 22, Polyquaternium 39, and Polyquaternium 47. Such polymers are, for example, copolymers consisting of dimethyldiallyl ammonium chloride and acrylic acid, terpolymers consisting of dimethyldiallyl ammonium chloride and acrylamide, and terpolymers consisting of acrylic acid methacrylamidopropyl trimethylammonium chloride and methyl acrylate such as those of the following formula wherein the ratio of n^6:n^7:n^8 is 45:45:10:



Highly preferred is Polyquaternium 47. Highly preferred commercially available amphoteric polymers herein include Polyquaternium 22 with tradenames MERQUAT 280, MERQUAT 295, Polyquaternium 39 with tradenames MERQUAT PLUS 3330, MERQUAT PLUS 3331, and Polyquaternium 47 with tradenames MERQUAT 2001, MERQUAT 2001N, all available from Calgon Corporation.

Also useful herein are polymers resulting from the copolymerisation of a vinyl monomer carrying at least one carboxyl group, such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, fumaric acid, crotonic acid, or alphachloroacrylic acid, and a basic monomer which is a substituted vinyl compound containing at least one basic nitrogen atom, such as dialkylaminoalkyl

methacrylates and acrylates and dialkylaminoalkylmethacrylamides and acrylamides.

Also useful herein are polymers containing units derived from:

i) at least one monomer chosen from amongst acrylamides or methacrylamides substituted on the nitrogen by an alkyl radical,

ii) at least one acid comonomer containing one or more reactive carboxyl groups, and

iii) at least one basic comonomer, such as esters, with primary, secondary and tertiary amine substituents and quaternary ammonium substituents, of acrylic and methacrylic acids, and the product resulting from the quaternisation of dimethylaminoethyl methacrylate with dimethyl or diethyl sulfate.

The N-substituted acrylamides or methacrylamides which are most particularly preferred are the groups in which the alkyl radicals contain from 2 to 12 carbon atoms, especially N-ethylacrylamide, N-tert.-butylacrylamide, N-tert.-octylacrylamide, N-octylacrylamide, N-decylacrylamide and N-dodecylacrylamide and also the corresponding methacrylamides. The acid comonomers are chosen more particularly from amongst acrylic, methacrylic, crotonic, itaconic, maleic and fumaric acids and also the alkyl monoesters of maleic acid or fumaric acid in which alkyl has 1 to 4 carbon atoms.

The preferred basic comonomers are aminoethyl, butylaminoethyl, N,N'-dimethylaminoethyl and N-tert.-butylaminoethyl methacrylates.

Commercially available amphoteric polymers herein include octylacrylamine/acrylates/butylaminoethyl methoacrylate copolymers with the tradenames AMPHOMER, AMPHOMER SH701, AMPHOMER 28-4910, AMPHOMER LV71, and AMPHOMER LV47 supplied by National Starch & Chemical.

<u>Poly α-Olefin Oil</u>

The composition of the present invention may further contain a poly α-olefin oil. The poly α-olefin oil herein provides an improved rinse feel by eliminating the ease of rinsing difficulties. It is believed that the poly α-olefin oil reduces the slicky/slimy feel of other conditioning agents by imparting a draggy feel to the hair when the hair is rinsed.

The poly α-olefin oil is preferably included in the composition at a level by weight of from about 0.1% to about 5%, preferably from about 0.5% to about 2%.

Poly α-olefin oils useful herein are those derived from 1-alkene monomers having from about 6 to about 16 carbons, preferably from about 6 to about 12 carbons atoms. Nonlimiting examples of 1-alkene monomers useful for preparing the poly α-olefin oils include 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, branched isomers such as 4-methyl-1-pentene, and mixtures thereof. Preferred 1-alkene monomers useful for preparing the poly α-olefin oils are 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and mixtures thereof. Poly α-olefin oils useful herein further have a viscosity of from about 1 to about 35,000 cst, a molecular weight of from about 200 to about 60,000, preferably less than 6,000, and more preferably 800; and a polydispersity of no more than about 3.

Particularly useful poly α-olefin oils herein include polydecenes with tradenames PURESYN 6 having a number average molecular weight of about 500, PURESYN 100 having a number average molecular weight of about 3000 and PURESYN 300 having a number average molecular weight of about 6000 available from Mobil Chemical Co.

<u>High Melting Point Compound</u>

The compositions may comprise a high melting point compound having a melting point of at least about 25°C selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, hydrocarbons, steroids, and mixtures thereof. Without being bound by theory, it is believed that these high melting point compounds cover the hair surface and reduce friction, thereby resulting in providing smooth feel on the hair and ease of combing. It is understood by the artisan that the compounds disclosed in this section of the specification can in some instances fall into more than one classification, e.g., some fatty alcohol derivatives can also be classified as fatty acid derivatives. However, a given classification is not intended to be a limitation on that particular compound, but is done so for convenience of classification and nomenclature. Further, it is understood by the artisan that, depending on the number and position of double bonds, and length and position of the branches, certain compounds having certain required carbon atoms may have a melting point of less than about 25°C. Such compounds of low melting point are not intended to be included in this section. Nonlimiting examples of the high melting point compounds are found in International Cosmetic Ingredient Dictionary, Fifth

Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, both of which are incorporated by reference herein in their entirety.

The fatty alcohols useful herein are those having from about 14 to about 30 carbon atoms, preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated. Nonlimiting examples of fatty alcohols include, cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.

The fatty acids useful herein are those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Also included are diacids, triacids, and other multiple acids which meet the requirements herein. Also included herein are salts of these fatty acids. Nonlimiting examples of fatty acids include lauric acid, palmitic acid, stearic acid, behenic acid, sebacic acid, and mixtures thereof.

The fatty alcohol derivatives and fatty acid derivatives useful herein include alkyl ethers of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, esters of fatty alcohols, fatty acid esters of compounds having esterifiable hydroxy groups, hydroxy-substitued fatty acids, and mixtures thereof. Nonlimiting examples of fatty alcohol derivatives and fatty acid derivatives include materials such as methyl stearyl ether; the ceteth series of compounds such as ceteth-1 through ceteth-45, which are ethylene glycol ethers of cetyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; the steareth series of compounds such as steareth-1 through 10, which are ethylene glycol ethers of steareth alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; ceteareth 1 through ceteareth-10, which are the ethylene glycol ethers of ceteareth alcohol, i.e. a mixture of fatty alcohols containing predominantly cetyl and stearyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; C_1-C_{30} alkyl ethers of the ceteth, steareth, and ceteareth compounds just described; polyoxyethylene ethers of behenyl alcohol; ethyl stearate, cetyl stearate, cetyl palmitate, stearyl stearate, myristyl myristate, polyoxyethylene cetyl ether stearate, polyoxyethylene stearyl ether stearate, polyoxyethylene lauryl ether stearate, ethyleneglycol monostearate, polyoxyethylene monostearate, polyoxyethylene distearate, propyleneglycol

monostearate, propyleneglycol distearate, trimethylolpropane distearate, sorbitan stearate, polyglyceryl stearate, glyceryl monostearate, glyceryl distearate, glyceryl tristearate, and mixtures thereof.

Hydrocarbons useful herein include compounds having at least about 20 carbons.

Steroids useful herein include compounds such as cholesterol.

High melting point compounds of a single compound of high purity are preferred. Single compounds of pure fatty alcohols selected from the group of pure cetyl alcohol, stearyl alcohol, and behenyl alcohol are highly preferred. By "pure" herein, what is meant is that the compound has a purity of at least about 90%, preferably at least about 95%. These single compounds of high purity provide good rinsability from the hair when the consumer rinses off the composition.

Commercially available high melting point compounds useful herein include: cetyl alchol, stearyl alcohol, and behenyl alcohol having tradenames KONOL series available from New Japan Chemical (Osaka, Japan), and NAA series available from NOF (Tokyo, Japan); pure behenyl alcohol having tradename 1-DOCOSANOL available from WAKO (Osaka, Japan), various fatty acids having tradenames NEO-FAT available from Akzo (Chicago Illinois, USA), HYSTRENE available from Witco Corp. (Dublin Ohio, USA), and DERMA available from Vevy (Genova, Italy); and cholesterol having tradename NIKKOL AGUASOME LA available from Nikko.

ADDITIONAL COMPONENTS

The shampoo compositions of the present invention may include a variety of additional components, which may be selected by the artisan according to the desired characteristics of the final product. Additional component include, for example, polyvalent metal cations, suspending agents, ethoxylated glucose derivatives, antidandruff agents, and other additional components.

Polyvalent Metal Cations

Suitable polyvalent metal cations include divalent and trivalent metals, divalent metals being preferred. Exemplary metal cations include alkaline earth metals, such as magnesium, calcium, zinc, and copper, and trivalent metals such as aluminum and iron. Preferred are calcium and magnesium.

The polyvalent metal cation can be added as an inorganic salt, organic salt, or as a hydroxide. The polyvalent metal cation may also be added as a salt with anionic surfactants as mentioned above.

Preferably, the polyvalent metal cation is introduced as an inorganic salt or organic salt. Inorganic salts include chloride, bromide, iodine, nitrate, or sulfate, more preferably chloride or sulfate. Organic salts include L-glutamate, lactate, malate, succinate, acetate, fumarate, L-glutamic acid hydrochloride, and tartarate.

It will be clear to those skilled in the art that, if polyvalent salts of the anionic surfactant is used as the mode of introducing the polyvalent metal cations into the compositions hereof, only a fraction of the anionic surfactant may be of polyvalent form, the remainder of the anionic surfactant being necessarily added in monovalent form.

Hardness of the conditioning shampoo compositions can be measured by standard methods in the art, such as by ethylene diamine tetraacetic acid (EDTA) titration. In the event that the composition contains dyes or other color materials that interfere with the ability of EDTA titration to yield a perceptible color change, hardness should be determined from the composition in the absence of the interfering dye or color.

Suspending Agents

A preferred additional component is a suspending agent, particularly for compositions comprising silicone compounds of high viscosity and/or large particle size. When present, the suspending agent is in dispersed form in the compositions. The suspending agent will generally comprise from about 0.1% to about 10%, and more typically from about 0.3% to about 5.0%, by weight, of the composition.

Preferred suspending agents include acyl derivatives such as ethylene glycol stearates, both mono and distearate, long chain amine oxides such as alkyl (C_{16}-C_{22}) dimethyl amine oxides, e.g., stearyl dimethyl amine oxide, and mixtures thereof. When used in the shampoo compositions, these preferred suspending agents are present in the composition in crystalline form. These suspending agents are described in U.S. Patent 4,741,855.

Other suitable suspending agents include alkanol amides of fatty acids, preferably having from about 16 to about 22 carbon atoms, more preferably about 16 to 18 carbon atoms, preferred examples of which include stearic

monoethanolamide, cocomonoethanolamide, stearic diethanolamide, stearic monoisopropanolamide and stearic monoethanolamide stearate.

Other suitable suspending agents include N,N-dihydrocarbyl amido benzoic acid and soluble salts thereof (e.g., Na and K salts), particularly N,N-di(hydrogenated) C_{16}, C_{18} and tallow amido benzoic acid species of this family, which are commercially available from Stepan Company (Northfield, Illinois, USA).

Other suitable suspending agents include xanthan gum. The use of xanthan gum as a suspending agent in silicone containing shampoo compositions is described, for example, in U.S. Patent 4,788,006, which is incorporated herein by reference in its entirety. Combinations of long chain acyl derivatives and xanthan gum may also be used as a suspending agent in the shampoo compositions. Such combinations are described in U.S. Patent 4,704,272, which is incorporated herein by reference in its entirety.

Other suitable suspending agents include carboxyvinyl polymers. Preferred among these polymers are the copolymers of acrylic acid crosslinked with polyallylsucrose as described in U.S. Patent 2,798,053, which is incorporated herein by reference in its entirety. Examples of these polymers include the carbomers, which are hompolymers of acrylic acid crosslinked with an allyl ether of pentaerythritol, an allyl ether of sucrose, or an allyl ether of propylene. Neutralizers may be required, for example, amino methyl propanol, triethanol amine, or sodium hydroxide.

Other suitable suspending agents can be used in the compositions, including those that can impart a gel-like viscosity to the composition, such as water soluble or colloidally water soluble polymers like cellulose ethers such as hydroxyethyl cellulose, hydroxymethyl cellulose, hydroxypropyl cellulose, and materials such as guar gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives.

<u>Ethoxylated Glucose Derivatives</u>

A preferred additional component is an ethoxylated glucose derivative, particularly for increasing the viscosity of compositions, and for the phase stability of compositions at high and low temperatures. When present, the ethoxylated glucose derivative is included at a level of from about 0.1% to about 10%, and more typically from about 0.3ٰ% to about 5.0%, by weight, of the composition.

Suitable ethoxylated glucose derivatives include methyl gluceth 10, methyl gluceth 20, PEG-120 methylglucose dioleate, PPG-10 methylglycose ether, and PPG-20 methylglycose ether. Commercially available material highly suitable herein include methyl gluceth 10 with tradename GLUCAM E-10, PEG-120 methylglucose dioleatewith tradename Glucamate DOE-120, PPG-10 methylglucose ether with tradename GLUCAM P-10, and PPG-20 methylglucose ether with tradename GLUCAM P-20, all available from Amerchol.

Antidandruff Agent

The present composition may contain a safe and effective amount of an antidandruff agent. When present, the antidandruff agent is typically used at a level from about 0.1% to about 5%, preferably from about 0.3% to about 5% by weight of the composition.

Without being bound by theory, it is believed that the coacervate made by the polyhydrophilic anionic surfactants and cationic conditioning agents of the present invention are also capable of trapping and effectively delivering the antidandruff agents herein to the hair surface.

Pyrithione salts are useful herein. Suitable pyrithione salts are heavy metal salts of 1-hydroxy-2-pyridinethione, the heavy metal salts being zinc, tin, cadmium, magnesium, aluminium, and zirconium. Preferred is zinc salt of 1-hydroxy-2-pyridinethione known in the art as zinc pyrithione, more preferably in a particle size of up to about 20 microns, still preferably from about 1 to about 10 microns. Commerically available pyrithione salts suitable herein include Zinc Pyrithione available from Olin.

Selenium sulfides are useful herein. Selenium sulfides herein include selenium disulfide, as well as Se_xS_y in cyclic structure, wherein x and y are integers and x + y equals 8. Preferred selenium sulfides are those having a particle size of less than about 15 microns, more preferably less than about 10 microns; wherein the particle size is measured by a laser light scatterring device such as Malvern 3600 instrument.

Sulfur and octopirox, its salts, and its derivatives are also useful herein.

Antidandruff agents as mentioned above can be used alone, or in combination with one another.

Other Additional Components

A wide variety of other additional ingredients can be formulated into the present compositions. These include: other conditioning agents such as

hydrolyzed collagen with tradename Peptein 2000 available from Hormel, vitamin E with tradename Emix-d available from Eisai, panthenol available from Roche, panthenyl ethyl ether available from Roche, hydrolysed keratin, proteins, plant extracts, and nutrients; emulsifying surfactants for dispersing water insoluble components in the carrier; hair-fixative polymers such as amphoteric fixative polymers, cationic fixative polymers, anionic fixative polymers, nonionic fixative polymers, and silicone grafted copolymers; optical brighteners such as polystyrylstilbenes, triazinstilbenes, hydroxycoumarins, aminocoumarins, triazoles, pyrazolines, oxazoles, pyrenes, porphyrins, and imidazoles; preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents such as the thioglycolates; perfumes; and sequestering agents, such as disodium ethylenediamine tetra-acetate; ultraviolet and infrared screening and absorbing agents such as octyl salicylate; and inorganic reducing agents such as sodium sulfite, sodium bisulfite, and potassium sulfite. Such optional ingredients generally are used individually at levels from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0% by weight of the composition.

EXAMPLES

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. Ingredients are identified by chemical or CTFA name, or otherwise defined below.

COMPOSITIONS OF EXAMPLES 1-6

Components	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex.6
N-cocoyl-L-glutamate *1	2	1	1.6	2	4	2
Disodium Lauryl Sulfosuccinate *2					1	
N-acyl-L- Aspartate *3			1			
Sodium Lauryl Aminodiacetic acid *4		1				

Cocamidopropylbetaine *5	2	3	1	2	1	2
Ammonium Laureth-3 Sulfate	10	10	10	10	10	10
Ammonium lauryl sulfate	2	2	2	2		2
Behenyl trimethylamonium chloride*6		0.25	0.1		0.5	
Polyquaterium-10 *7		0.5			1.0	
Silicone Emulsion-1 *9	0.5		3.0		2.5	2.0
Silicone Emulsion-2 *13		3.33		2.0		
Puresyn 6		0.1	2.0		1.0	
Stearyl Betaine *11		0.5	0.25	1.0	1.0	
Oleyl Betaine *12		1.0				
Stearyl Dihydroxyethyl Betaine *14			1.0		0.5	
Cetyl Alcohol	1.0		0.5		1	1
Cocamide MEA	1.5	1.5	1.5	1.5	1.5	1.5
Polyquaterium-47 *8		0.5	0.2		0.5	
Ethylene Glycol Distearate	1.5	3.0	1.5	1.5		1.5
Perfume solution	0.5	0.5	0.5	0.5	0.5	0.5
DMDM Hydantoim		0.2	0.37	0.37	0.37	
Kathon CG	0.05	0.02		0.033	0	0.034
PEG120 Methyl Glucose Dioleate *10		0.5	0.2		1.5	
d- delta Tocopherol	0.1		0.2		0.1	0.1
Tocopherol acetate		0.1		0.2		
Panthenol	0.2	0.1	0.1	0.1		
Pantyl B	0.2	0.1	0.2	0.2		
Sodium sulfite	0.01	0.01	0.05	0.1		
Parsol MCX		1.0	0.1	0.5	2.0	
Benzophenone	0.01	1.0	0.2			
Peptein 2000	0.01	0.1	0.01			
$MgCl_2$		0.5	0.2		0.1	
$MgSO_4$		0.5				
Deionized Water	----------------q.s. to 100%----------------					

COMPOSITIONS OF EXAMPLES 7-8

Components	Ex. 7	Ex.8
N-acyl-L- Aspartate *3	5	
Sodium Lauryl Aminodiacetic acid *4		5

Cocamidopropylbetaine *5	5	5
Ammonium Laureth-3 Sulfate	10	10
Ammonium lauryl sulfate	5	2
Behenyl trimethylamonium chloride*6	0.5	0.5
Polyquaterium-47 *8	0.2	0.2
Polyquaterium-10 *7	0.5	0.5
Puresyn 6	2.0	0.25
Silicone Emulsion-1 *9	4.0	3.0
Stearyl Betaine *11		1.0
Stearyl Dihydroxyethyl Betaine *14	1.0	
Zinc Pyrithion *15	1.0	1.0
Cocamide MEA	1.5	1.5
Ethylene Glycol Distearate	1.5	1.5
Perfume solution	0.5	0.5
DMDM Hydantoim		0.37
Kathon CG	0.04	
PEG120 Methyl Glucose Dioleate *10		1.0
Hydrolyzed Collagen *16	0.01	
Vitamin E *17		0.01
Panthenol *18		0.025
Pantheny Ethyl Ether *19		0.025
Tocopherol acetate		0.2
Panthenol	0.1	0.1
Sodium sulfite	0.05	0.1
Peptein 2000	0.01	
Parsol MCX	0.1	0.5
Benzophenone	0.2	0.2
Deionized Water	q.s. to 100%	

DEFINITIONS OF COMPONENTS

*1 N-cocoyl-L-glutamate: Amisoft CT-12S available from Ajinomoto.

*2 Disodium Lauryl Sulfosuccinate: Emcol 4400-1 available from Witco

*3 N-acyl-L- Aspartate: Asparak available from Mitsubishi

*4 Sodium Lauryl Aminodiacetic acid: Nissan Anon LA available from Nippon Oil and Fat

*5 Cocamidopropylbetaine: Tego Betaine F available from TH Goldschmidt

*6 Behenyl trimethylamonium chloride: Econol TM22 available from Sanyo Kasei

*7 Polyquaterium-10: UCare Polymer JR400 available from Amerchol

*8 Polyquaterium-47: Merquat 2001 available from Calgon

*9 Silicone Emulsion-1: mechanically emulsified emulsion containing made using16.2% polydimethylsiloxane having about 900 repeating units, 43.8% polydimethylsiloxane having about 100 repeating units, and 3.0% stearyl trimonium chloride, wherein the silicone compound has a particle size of about 250nm and the viscosity of the emulsion is approximately 60000 cPs available from Dow Corning Silicone

*10 PEG120 Methyl Glucose Dioleate: Glucamate DOE-120 available from Amerchol

*11 Stearyl Betaine: Rikabion A-700 available from New Japan Chemical

*12 Oleyl Betaine: Rikabion A-300 available from New Japan Chemical

*13 Silicone Emulsion-2: mechanically emulsified emulsion containing made using 14.85% polydimethylsiloxane having about 900 repeating units, 40.15% polydimethylsiloxane having about 100 repeating units, and 6.0% stearyltimonium chloride, wherein the silicone compound has a particle size of about 250nm and the viscosity of the emulsion is approximately 60000 cPs available from Dow Corning Silicone

*14 Stearyl Dihydroxyethyl Betaine: Anon AB 202 available from Nihon Oil & Fats

*15 Zinc Pyrithion: available from Olin

*16 Hydrolyzed Collagen: Peptein 2000 available from Hormel

*17 Vitamin E: Emix-d available from Roche

*18 Panthenol: available from Roche

*19 Pantheny Ethyl Ether: available from Roche

<u>METHOD OF PREPARATION</u>

The shampoo compositions of Examples 1 through 8 as shown above can be prepared by any conventional method well known in the art. Suitable methods are described below.

Polymers and surfactants are dispersed in water to form a homogenous mixture. To this mixture are added the other ingredients except for cationic silicone emulsion, perfume, and salt; the obtained mixture is agitated. The

obtained mixture is then passed through a heat exchanger to cool, and the cationic silicone emulsion, perfume, and salt are added. The obtained compositions are poured into bottles to make hair shampoo compositions. Alternatively, water and surfactants and any other solids (except cationic silicone emulsion) that need to be melted can be mixed together at elevated temperature, e.g., above about 70°C, to speed the mixing into shampoo. Additional ingredients can be added either to this hot premix or after cooling the premix. The ingredients are mixed thoroughly at the elevated temperature and then pumped through a high shear mill and then through a heat exchanger to cool them to ambient temperature. Then the cationic silicone emulsion is added at room temperature to the cooled mix and mixed well.

The embodiments disclosed and represented by the previous examples have many advantages. For example, they can provide improved conditioning benefit when the hair is dried such as prevention of fly away, ease of combing, and soft and moist feeling.

It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from its spirit and scope.

WHAT IS CLAIMED IS:

1. A conditioning shampoo composition comprising by weight:
(a) from about 0.05% to about 50% of a polyhydrophilic anionic surfactant;
(b) from about 0.05% to about 20% of a cationic conditioning agent selected from the group consisting of cationic surfactants, cationic polymers, and mixtures thereof;
(c) from about 0.2% to about 20% of a cationic silicone emulsion comprising by weight of the cationic silicone emulsion from about 2% to about 20% of a cationic surfactant; and an emulsifiable amount of a silicone compound having a particle size of less than about 50 microns; and
(d) an aqueous carrier.

2. The conditioning shampoo composition according to Claim 1 wherein the cationic silicone emulsion comprises from about 2% to about 8% of the cationic surfactant.

3. The conditioning shampoo composition according to Claim 1 wherein the cationic silicone emulsion comprises from about 4% to about 8% of the cationic surfactant.

4. The conditioning shampoo composition according to Claim 2 or 3 wherein the silicone particle has a particle size of from about 0.2 microns to about 2.5 microns.

5. The conditioning shampoo composition according to Claim 4 wherein the silicone compound comprises a mechanically emulsified polydimethylsiloxane.

6. The conditioning shampoo composition according to Claim 5 wherein the silicone compound comprises a highly viscous polydimethylsiloxane and a low viscosity polydimethylsiloxane.

7. The conditioning shampoo composition according to Claim 4 wherein the silicone compound comprises an emulsion polymerized hydroxy-endcapped polydimethylsiloxane.

8. The conditioning shampoo composition according to Claim 1 further comprising by weight:

(e) from about 0.2% to about 10% of a betaine conditioning agent;

(f) from about 0.01% to about 5% of an amphoteric polymer; and

(g) from about 0.1% to about 5% of a poly α-olefin oil derived from 1-alkene monomers having from about 6 to about 16 carbons, the poly α-olefin oils having a viscosity of from about 1 to about 35,000 cst, a molecular weight of from about 200 to about 60,000, and a polydispersity of no more than about 3.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/09097

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/50 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 29094 A (UCHIYAMA HIROTAKA ;HU FANG (JP); HARADA KIROH (JP); SAKO TAKASHI ()) 9 July 1998 (1998-07-09) page 35; examples 1,5	1
X	WO 99 13839 A (UCHIYAMA HIROTAKA ;EGOSHI YASUHIRO (JP); SAKO TAKASHI (JP); PROCTE) 25 March 1999 (1999-03-25) page 38; examples	1
X	WO 96 32919 A (PROCTER & GAMBLE) 24 October 1996 (1996-10-24) the whole document	1
X	EP 0 612 514 A (DOW CORNING) 31 August 1994 (1994-08-31) the whole document	1
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 January 2000	01/02/2000

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/09097

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 99/09097

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